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Water Quality Interpretive Report No.4

PESTICIDE MONITORING IN THE PRAIRIES OF WESTERN CANADA,
1979.

Pesticide Monitoring in the Prairies of Western Canada

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WATER QUALITY INTERPRETIVE REPORT NO. 4
(Résumé en français)

Canada

**INLAND WATERS DIRECTORATE,
WESTERN AND NORTHERN REGION,
WATER QUALITY BRANCH,
REGINA, SASKATCHEWAN, 1979.**

Cover photograph —
Pesticide spraying, Beavers Hill Community Pasture, North Battleford
Area, 1957. Courtesy of Prairie Farm Rehabilitation Administration.



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Pesticide Monitoring in the Prairies of Western Canada

William D. Gummer

*Paper presented at the International Symposium on the
Analysis of Hydrocarbons and Halogenated Hydrocarbons,
Burlington, Ontario, May 1978.*

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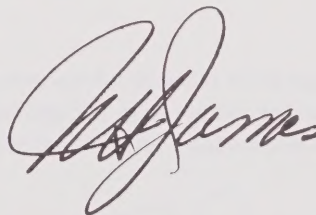
Foreword

Canada is a land richly endowed with fresh water contained in a myriad sparkling streams and lakes as well as large navigable rivers. It is becoming clear, however, that our water resources are not limitless and that some areas are even now in danger of running short of useable water. Along with a growing awareness that our water resources are limited in certain areas of Canada, concerns for the *quality* of the water throughout Canada are rapidly developing.

Most water uses, be they recreational, agricultural, industrial, or domestic, have very specific requirements for the quality of the water resource. In many instances, the water quality dictates the limitations on the use of a water resource. Therefore, the quality of a water resource can have profound implications on the social and economic development of an area.

Fisheries and Environment Canada has monitored the quality of many of Canada's major surface waters for a number of years. The National Monitoring Program carried on by the Water Quality Branch of the department has varied over the years but has gradually expanded to include approximately one thousand sampling sites, which reflect national, regional, and local water quality concerns. The data are stored on NAQUADAT, the data processing system of the Branch, and are periodically published in summary form in the Water Quality Data series. Although these summaries have proven valuable as reference data sources, it has been realized that these reports can only be fully utilized by persons familiar with the interpretation of water quality data. In order to involve a wider audience in the appreciation of water quality data, this new series, Water Quality Interpretive Reports, has been produced. This report and future ones will parallel the Water Quality Data reports. It is anticipated that this type of report will extend the basic understanding of water quality by utilizing the existing historical water quality data which have been collected by both federal and provincial agencies and entered onto NAQUADAT. These reports will emphasize pertinent water quality information through the use of graphical, tabular, and concise textual presentations.

Individual reports will aim at interpreting regional water quality data for a broad spectrum of uses. It is hoped that these reports will be informative and useful to the public and resource planners.



N.H. James
Director General
Inland Waters Directorate

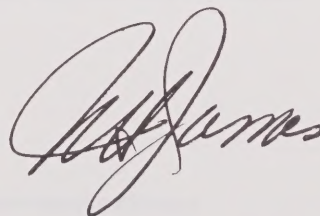
Avant-propos

Le Canada est un pays pourvu de vastes réserves d'eau douce emmagasinées dans une myriade de rivières et lacs miroitants ainsi que grands cours d'eau navigables. Il devient toutefois évident qu'il existe une limite à nos ressources en eau et que certains endroits au pays sont menacés, à l'instant même, par une pénurie d'eau propre. En même temps que s'effectue cette prise de conscience accrue en ce qui concerne la disponibilité des ressources en eau dans les régions données du pays, l'intérêt suscité par la *qualité* des eaux augmente considérablement à travers le Canada.

La plupart des utilisations de l'eau, à savoir récréatives, agricoles, industrielles ou domestiques, ont des normes bien définies en matière des ressources en eau. Dans bien des cas, la qualité des eaux gouverne les exigences des utilisations possibles des ressources en eau. En fait, la qualité de ses ressources en eau peut avoir des significations profondes sur le développement économique et social d'une région.

Le ministère des Pêches et de l'Environnement du Canada surveille, depuis maintes années, la qualité de plusieurs nappes d'eau de surface importantes au pays. Le programme national de surveillance mis en oeuvre par la Direction de la qualité des eaux du Ministère, a varié en importance au cours des années et s'est graduellement étendu à environ mille stations d'échantillonnage qui reflètent toutes les intérêts nationaux, régionaux et locaux en matière de qualité des eaux. Les données sont emmagasinées dans la banque NAQUADAT, système d'automatisation des données de la Direction, et sont publiées à intervalle régulier sous forme d'extraits dans la série des *Données sur la qualité des eaux*. Quoiqu'utiles en tant que sources de données de base, les extraits semblent principalement destinés aux utilisateurs connaissant les modes d'interprétation des données sur la qualité des eaux. C'est pour encourager la dissémination des données sur la qualité des eaux et améliorer la compréhension d'un public bien informé, que la présente collection intitulée *Water Quality Interpretive Reports* est publiée. Le présent rapport ainsi que les autres qui paraîtront égaleront les rapports de la série des *Données sur la qualité des eaux*. Un rapport de ce genre tente de faire mieux connaître les divers éléments de la qualité des eaux en ayant recours aux données historiques actuelles recueillies à la fois par des organismes fédéraux et provinciaux et enregistrées dans la banque NAQUADAT. Les nouveaux rapports vont mettre en relief l'information qui a rapport à la qualité des eaux en s'appuyant sur des graphiques, des tableaux et un texte clair et consis.

Chaque rapport constituera une interprétation des données sur la qualité des eaux régionales en fonction d'une gamme d'utilisations possibles. De cette façon, les rapports seront du genre didactique et pourront être utilisés par le grand public et les responsables de la gestion des ressources en eau.



N.H. James
Directeur général
Direction générale des eaux intérieures

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Abstract

Pesticide monitoring programs conducted by the Water Quality Branch of the Department of the Environment during the period 1971 to 1977 revealed a widespread distribution of 2,4-D; 2,4,5-T; γ -BHC (lindane); and α -BHC as well as a more limited distribution of 2,4-DP (dichloroprop); aldrin; and β -Endosulfan in surface waters of western Canada.

Atmospheric transportation and deposition are the mechanisms believed responsible for the wide distribution of lindane and α -BHC in western Canada. It is speculated that isomerization of lindane to the α -BHC isomer accounts for the abundance of α -BHC. Concentrations of both lindane and α -BHC at times exceeded 0.01 $\mu\text{g/L}$. The herbicide 2,4-D was observed to be prevalent in the agricultural areas at concentrations above 0.01 $\mu\text{g/L}$ and as high as 4.33 $\mu\text{g/L}$. In addition to agriculture, industries and municipalities were found to contribute pesticides to the aquatic environment.

Résumé

Des programmes de contrôle des pesticides menés par la Direction de la qualité des eaux du ministère de l'Environnement de 1971 à 1977 ont révélé des quantités répandues de 2,4-D, de 2,4,5-T, de γ -BHC (lindane) et de α -BHC, de même qu'une quantité plus limitée de 2,4-DP (dichloroprop), d'aldrin et de β -Endosulfan dans les eaux de surface de l'ouest canadien.

On croit que la quantité répandue de lindane et de α -BHC dans l'ouest du Canada doit être attribuée aux mécanismes de transport atmosphérique et de dépôt. On suppose que l'isomérisation du lindane à l'isomère α -BHC explique l'abondance de α -BHC. À quelques reprises, la concentration de lindane et de α -BHC dépassait 0.01 $\mu\text{g/L}$. On a remarqué que l'herbicide 2,4-D était surtout répandu dans les régions agricoles, où son taux de concentration était supérieur à 0.01 $\mu\text{g/L}$ et s'élevait même jusqu'à 4.33 $\mu\text{g/L}$. En plus de l'agriculture, on a découvert que les industries et les municipalités causaient l'infiltration des pesticides dans l'environnement aquatique.

Pesticide Monitoring in the Prairies of Western Canada

William D. Gummer

INTRODUCTION

Environmental Concern

Public awareness and concern about the quality of the environment in which man coexists with all other forms of life have increased considerably during the last 15 years. Pesticide-induced environmental degradation constitutes part of this concern, the magnitude of which was uncovered in the early sixties by such authors as Carson (1962) and Rudd (1964). Edwards (1973) presents information on the amounts of residues in the environment and lists relevant reviews and symposia on the persistence of pesticides in the environment. The Canadian Wildlife Service (1971) confirms that Canada has not escaped environmental contamination from pesticides, and that nearly all the samples of Canadian wildlife (mammals, fish, fish food, marine invertebrates, migratory and non-migratory birds) analyzed during a 5-year study contained pesticide residues.

The concentrations of pesticides in water have become a major concern because water is a basic sustainer of life. The health of all life forms can thus be affected by pesticides in water. Because of this and because of the requirement for water of good quality for most human, industrial, agricultural and recreational activities, the Water Quality Branch, Inland Waters Directorate, Environmental Management Service, Environment Canada, conducts a program to measure and assess water quality in Canada.

Environmental Sources and Pathways

Edwards (1973) states that direct and indirect applications of pesticides, agricultural runoff, and industrial discharges are the principal sources of pesticide residues to surface waters. Although it is extremely difficult to qualify, the domestic and municipal use of pesticides undoubtedly contributed significantly to surface water contamination. It is estimated that in 1970-1971, urban home and garden use accounted for about 24% of the pesticide market in Alberta (Alberta Environment Conservation Authority, 1973); this probably typifies domestic use and national scale as well. The unregulated and likely indiscriminate domestic use of pesticides poses a threat to the health of man and the environment.

Pesticides may enter the aquatic environment directly. The direct application of the chemicals DDT and methoxychlor to surface waters has occurred in the Prairies to control mosquito and black fly infestations. Fredeen *et al.* (1970) reported that the Saskatchewan River (North and South) was treated with 3436 kg DDT for the control of black flies. The herbicide 2,4-D (butoxyethylester) is registered in Canada for the control of aquatic weeds, although the extent of aquatic use in western Canada is not known.

Some industrial sources of pesticides in western Canada are the pulp and paper industry, pesticide packaging plants, pesticide manufacturing plants, the food industry, and the seed dressing industry.

Agriculture is the largest single user of pesticides which are essential for high agricultural productivity and for the control of insect-borne diseases. The high level of agricultural activity in western Canada has resulted in the use of a variety of pesticides which have the potential to seriously degrade the natural environment.

When pesticides are applied in agricultural areas, small amounts drift into the atmosphere and are deposited in remote areas, contaminating both the hydrosphere and the biosphere. Water transport of pesticides is chiefly through surface runoff, which may cause contamination of low-lying areas and of water bodies (Gerakis and Sticas, 1974).

The dissipation and mobility of pesticides in the environment are contingent upon numerous factors, many of which are illustrated in Figure 1.

Invariably, the aquatic environment is the ultimate recipient of pesticides applied to the land and those released from industry and urban developments. The sources of pesticides to the environment are well known and are controllable. However, the fate of these pesticides in the environment is considerably less known and virtually uncontrollable. Some of the known processes that influence the fate of pesticides are noted in Table 1.

Once in the aquatic environment, pesticides may be volatilized, remain in solution or suspension, precipitate

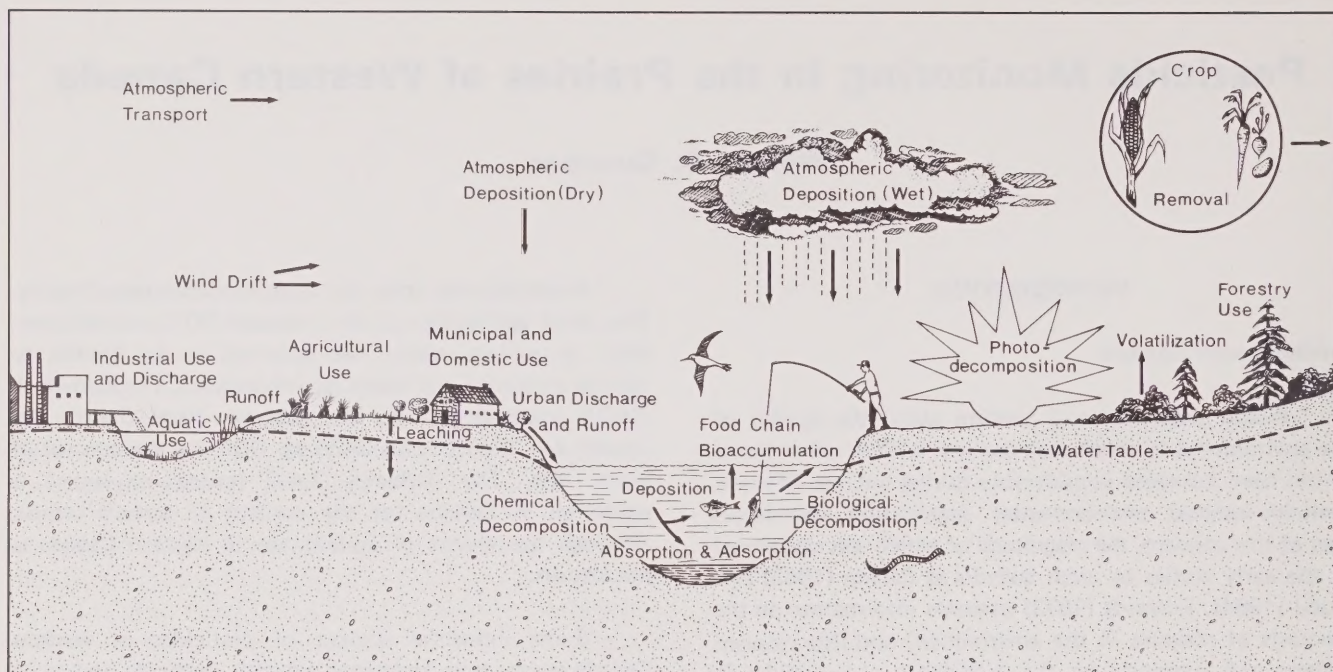


Figure 1. Pesticide uses and environmental pathways.

with and as sediment, or be assimilated by biota in the ecosystem. Most pesticides are insoluble or slightly soluble in water and therefore tend to accumulate in bottom sediments, with the result that concentrations in sediments are generally much higher than in the surrounding water. Gerakis and Sticas (1974) report that the accumulation of pesticides in bottom sediments play an important role in the disappearance of pesticides from contaminated water. They support this by stating that studies in major agricultural river basins in California revealed that an average pesticide concentration of 0.1 $\mu\text{g/L}$ to 0.2 $\mu\text{g/L}$ in river water may indicate that bottom sediments contain 20 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$. Bottom sediments are therefore a sink for these toxic substances, posing not just an immediate threat but also a threat to the aquatic environment over time.

Recognizing that sediments accumulate pesticides, the Water Quality Branch chose however to monitor the water phase in order to better understand the distribution, abundance and movement of pesticides in surface waters of western Canada. In addition, it was felt that any contamination of the aquatic environment would be at least detectable in the water phase, the phase more easily collected and analyzed. The results of monitoring this phase is the topic of this report.

Toxicological Properties

The toxicological effects of pesticides on aquatic life are well documented (U.S. Office of Science and Technology, 1971). Pesticides generally have deleterious effects on aquatic life, wildlife and man. Yet the toxicological properties of the individual pesticides differ considerably. Most pesticides are toxic to most forms of life even at low concentrations, and some are known to be carcinogenic. Certain pesticides, typically the organochlorine pesticides, persist in the aquatic environment and remain a threat over a long period of time. These pesticides are generally considered to be hazardous to fish and other aquatic life and are slightly to highly bioaccumulative. The Canada Department of Agriculture has placed restrictions and/or suspensions on many of the persistent organochlorine pesticides. Weber (1977) reports that the mobility of this group of pesticides ranges from the relatively non-mobile,

Table 1. Factors Influencing the Fate of Pesticides.

Physio-Chemical	Biological	Other
solubility	bioaccumulation	runoff /precipitation
co-distillation	biodegradation	management practices
volatility	biouptake	wind-drift
photodegradation	bioavailability	erosion
stability		
temperature		
active life		
sorption		
formulation		

non-volatile chemicals, such as DDT, to the highly mobile, moderately volatile chemicals, such as γ -BHC (lindane).

Weber (1977) also reports that the organophosphorus insecticides, although more toxic to man, are less toxic to fish than the organochlorine group. He states further that organophosphorus insecticides are more soluble, have a lesser tendency to bioaccumulate and are only slightly more mobile than organochlorine pesticides. Their mobility is restricted because of their tendency to complex with soil colloids.

Weber states that carbamate insecticides (carbofuran and "Baygon") have toxicological characteristics similar to the organophosphorus insecticides. Carbamate insecticides, however, have not been as fully researched as the others. He says that the chlorophenoxy acid herbicides such as 2,4-D and 2,4,5-T are considerably less toxic than the pesticides above and that these degrade rapidly in the environment. The mobility of this group is less than that of the organochlorine pesticides.

The Pesticide Monitoring Program

In response to environmental concerns, the monitoring of pesticides in water commenced in 1971. The initial

program was *ad hoc*, and because of resource limitations, water sampling was done only after spraying activities and primarily only on waters most likely affected. In 1973 a well-defined ongoing pesticide monitoring program evolved. Thirty-eight strategically selected pesticide sites (Figure 2) were established throughout the prairie region of Canada, with emphasis on monitoring the quality of interjurisdictional waters. The designated pesticide sites were sampled quarterly. In late 1976, monthly sampling for 2,4-D and 2,4,5-T began at the designated interprovincial locations.

Special surveys carried out in addition to the regular monitoring program broadened the regional pesticide data base. Data derived from other programs jointly financed with other agencies were also available. This report presents the findings of the aforementioned monitoring programs for the 1971-1977 period, and includes more than 20 000 pesticide analyses. Pesticides that have been investigated during this period are shown in Table 2. This report focuses on the five pesticides [2,4-D; 2,4,5-T; 2,4-DP (dichloroprop); lindane; and α -BHC] that are most commonly detected in the surface waters of western Canada.

METHODOLOGY

All water samples collected are defined as "grab samples" and were collected in accordance with Water Quality Branch sampling procedures (Environment Canada, 1973; Water Quality Branch, 1976). Each pesticide reflects an instantaneous concentration at a particular place at a particular time. The data herein refer to the total dissolved fraction plus that portion associated with the suspended particles.

The pesticides monitored were analyzed for the most part in accordance with Water Quality Branch procedures (Environment Canada, 1974).

Water samples for pesticide analyses were collected in acid pre-cleaned 1.2 L glass bottles. At the time of collection, samples for chlorophenoxy acid herbicides and carbamate insecticides were acidified to pH 2 with either sulphuric or hydrochloric acid; samples for organophosphorus pesticides were acidified to pH 4 with hydrochloric acid. All bottles were tightly capped with an aluminum foil-lined top and stored at 4°C in darkness until analyzed.

Organochlorine samples were extracted with pesticide-residue grade hexane by mechanical vortexing at room temperature. The extract was concentrated to 1 mL and fractionated using the *Florisil* column procedure or by the preparative high speed liquid chromatography using a stainless steel column (1.22 m x 0.64 cm OD) packed with

Table 2. Pesticides and Metabolites Investigated.

Pesticide Group	Compounds Investigated*
Organochlorine	aldrin α -BHC γ -BHC (lindane) p, p'-DDD p, p'-DDE p, p'-DDT dieldrin α -Endosulfan β -Endosulfan endrin heptachlor heptachlor epoxide p, p'-methoxychlor
Chlorophenoxy acid	2,4-D 2,4-DB 2,4-DP 2,4,5-T MCPA
Organophosphorus	dimethoate Guthion malathion
Carbamates	Baygon carbofuran

*Capitalized name indicates a brand name

Porasil "a" (37-75 μm). Isocratic elutions of step-wise increasing polarity yielded four fractions which were concentrated and analyzed by isothermal, electron capture gas chromatography.

Chlorophenoxy acid herbicide samples were extracted with methylene chloride. The extract was dried using acidic sodium sulphate; the methylene chloride was sequentially replaced with methanol and the solution concentrated to 1 mL. The extracted residues were derivatized to form one of the methyl, 2-chloroethyl or pentafluorobenzyl esters. The derivatives were fractionated and the excess reagent removed by column chromatography with neutral alumina (when required). The concentrate was analyzed by isothermal, electron capture gas chromatography.

Sodium sulphate was added to the water samples requiring carbamate analysis. The sample was then extracted with methylene chloride. The extract was concentrated to 1 mL and analyzed using a nitrogen detector.

Sodium sulphate was added to the water samples requiring organophosphorus pesticide analysis. The sample was then extracted with pesticide-residue grade benzene by mechanical vortex stirring at room temperature. The extract was decanted, concentrated and analyzed by isothermal gas chromatography using sulphur and phosphorus specific flame photometric detection.

RESULTS AND DISCUSSION

To facilitate discussion of the pesticide data, the Prairie Provinces have been divided into 14 water quality districts (Figure 2), taking into consideration river basin drainage (Water Survey of Canada, 1974), vegetation forms and the physiographic regions of Canada (Surveys and Mapping Branch, 1973).

The water quality districts are:

- I Mountain
- II Missouri River
- III Western South Saskatchewan River
- IV Red Deer River
- V North Saskatchewan River
- VI Peace — Athabasca
- VII Cold Lake — Lac la Ronge
- VIII Saskatchewan River
- IX Eastern South Saskatchewan River
- X Qu'Appelle River
- XI Souris River
- XII Red River
- XIII Assiniboine River — Red Deer River
- XIV Canadian Shield

The shaded portion of the inset map on Figure 2 (land classes 1-3) corresponds closely with the grasslands areas, and the unshaded portion corresponds with the woodland areas of the vegetation regions of Canada (Surveys and Mapping Branch, 1973). The land classes 1-3 are considered indicative of the prime grain production areas and are thus indicative of the area of greatest pesticide diversity and use. The woodland area (the unshaded area in inset map, Figure 2) on the other hand, hosts a smaller variety of pesticides which are related to the pulp and paper, and the livestock industries; the use of crop pesticides is considerably less and is scattered in this area.

Organochlorine Insecticides

Organochlorine insecticides have been used extensively in western Canada; however, their use has diminished considerably over the past few years. The organochlorine insecticides and some of their metabolites investigated in surface waters of western Canada are shown in Table 2. These pesticides are presently registered, but their use is restricted and limited.

Approximately 1400 samples were analyzed for 13 organochlorine residues (Table 2) in the surface waters of western Canada, and only lindane, α -BHC, heptachlor, aldrin and β -Endosulfan were detected. Only seven positive detections out of 1425 tests for heptachlor were observed. These occurred in districts III and X of the grasslands and were between 0.001 $\mu\text{g/L}$ and 0.007 $\mu\text{g/L}$.

Slightly more than 1400 tests were performed for aldrin and β -Endosulfan. Only two positive detections for aldrin are on record, one in the North Saskatchewan River system (district V) and one in the Qu'Appelle River system (district X) at levels of 0.005 $\mu\text{g/L}$ and 0.002 $\mu\text{g/L}$, respectively. Beta-Endosulfan was detected only once, in March 1973, at a level of 0.011 $\mu\text{g/L}$ in the Manitoba portion of the Souris River district (XI).

The lack of detection of these organochlorine residues in surface waters can be explained for the most part by the reduction in use over the last few years of these persistent pesticides and most importantly by the fact that these pesticides tend to accumulate in the sediment.

Lindane is registered in Canada for (1) controlling ticks and flies on livestock, (2) seed treatment for wire-worm control, (3) controlling infestations of stored logs by the logging industry, and (4) controlling bedbugs by the pest control industry. Additional uses are on nursery stocked trees, as soil treatment, in dog pounds for control of fleas, in farm buildings (wall spraying), and in warehouses where food is not stored.

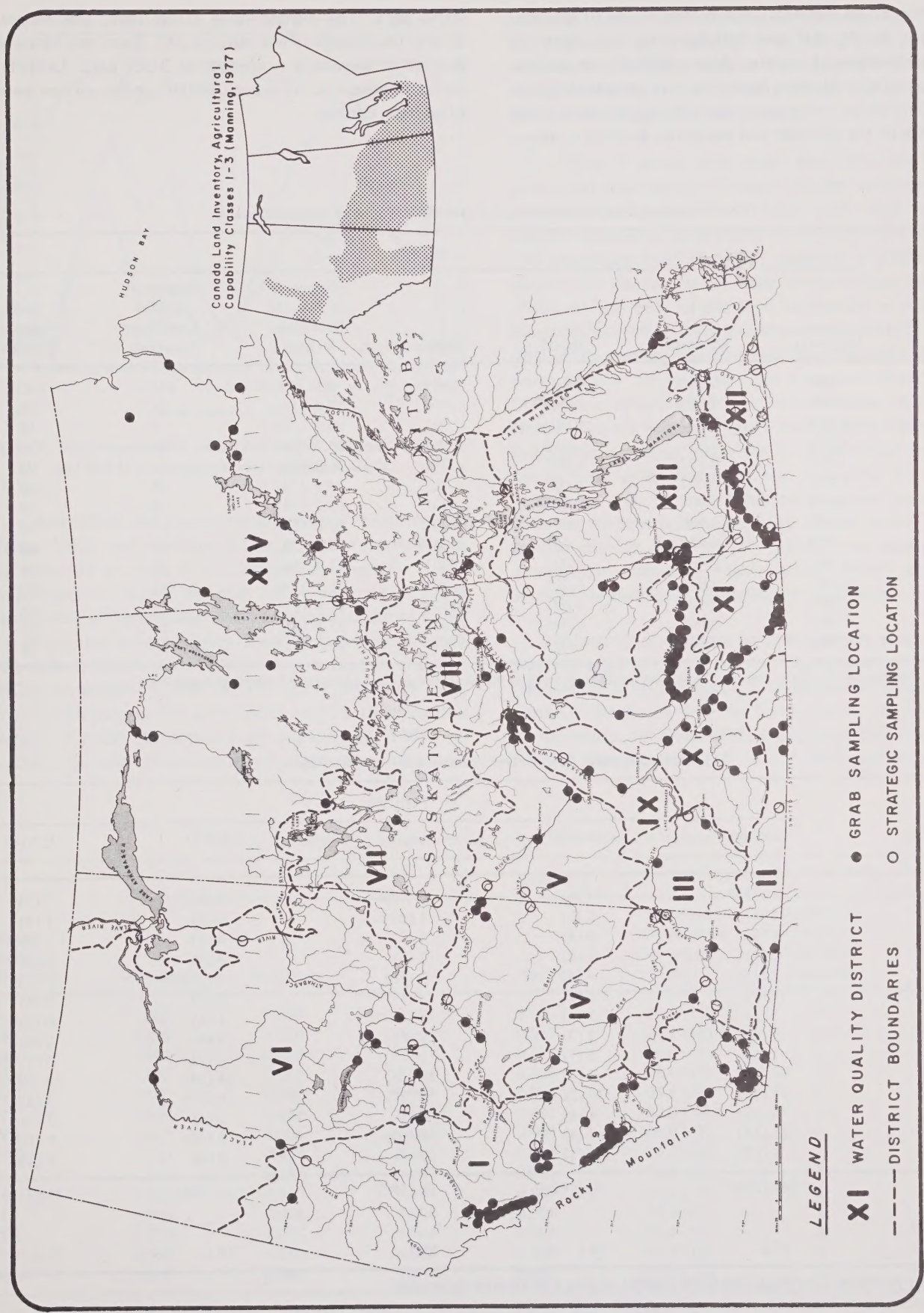


Figure 2. Pesticide sampling locations (inset map indicates prime grain production areas).

Table 3 and Figure 3 indicate that of the 14 districts, II, III, IX, X, XI, XII and XIII have the most frequent positive detections of lindane. About 58% of the stations monitored (Table 4) were found to have detectable quantities of lindane at one or more times during the monitoring period. Six of the districts had maximum levels at or above

0.005 µg/L. The highest value, 0.086 µg/L, was recorded in the Qu'Appelle River district (X). Even the Mountain district (I) showed a maximum of 0.007 µg/L. Lindane is not as prevalent as its isomer, α-BHC, in the surface waters of western Canada.

Table 3. Lindane Concentrations (µg/L) in Surface Waters of Western Canada

Water Quality Districts	Statistics				Frequency of Possible Detections % (No.)	Number of Values Less Than Detection	Total Number of Tests
	Minimum	Maximum	Mean*	Median			
I	<.001	0.007	<.001	<.001	6.1 (38)	585	623
II	<.001	0.003	0.001	<.001	50.0 (14)	14	28
III	<.001	0.002	0.001	<.001	50.0 (9)	9	18
IV	<.001	0.005	<.001	<.001	20.7 (16)	61	77
V	<.001	0.002	<.001	<.001	26.0 (25)	71	96
VI	<.001	0.002	<.001	<.001	9.5 (4)	38	42
VII	<.001	0.001	<.001	<.001	18.2 (4)	18	22
VIII	<.001	0.008	0.001	<.001	28.8 (17)	42	59
IX	<.001	0.010	<.001	<.001	49.2 (32)	33	65
X	<.001	0.086	<.001	<.001	47.9 (90)	98	188
XI	<.001	0.004	0.001	0.001	47.3(104)	116	220
XII	<.001	0.003	<.001	<.001	45.8 (21)	27	48
XIII	<.001	0.008	0.001	<.001	33.3 (41)	82	123
XIV	<.001	0.002	<.001	<.001	30.5 (11)	25	36

* The computation of the mean assumes "less than" values as real and equal to the analytical detection limit minus 0.0001 µg/L

Table 4. Sites with Positive Detections for Selected Pesticides.

Water Quality District	Pesticides				
	Lindane	α-BHC	2, 4, 5-T	2, 4-D	2, 4-DP
I	27 (78)*	44 (48)	8 (73)	5 (72)	2 (74)
II	3 (6)	5 (5)	1 (6)	5 (6)	1 (4)
III	6 (9)	4 (4)	4 (8)	8 (8)	5 (8)
IV	3 (3)	2 (2)	2 (3)	3 (3)	0 (3)
V	9 (16)	4 (4)	7 (13)	13 (13)	5 (13)
VI	2 (9)	2 (2)	4 (7)	5 (7)	3 (8)
VII	1 (3)	1 (1)	1 (1)	1 (1)	0 (2)
VIII	5 (8)	3 (3)	5 (6)	6 (6)	2 (6)
IX	1 (6)	1 (1)	1 (1)	1 (1)	0 (1)
X	44 (59)	3 (3)	28 (35)	24 (24)	22 (39)
XI	27 (27)	20 (20)	3 (27)	26 (27)	3 (27)
XII	4 (4)	4 (4)	3 (4)	4 (4)	2 (4)
XIII	11 (11)	4 (4)	5 (10)	9 (10)	1 (10)
XIV	6 (19)	1 (1)	9 (4)	0 (4)	0 (16)
Total	149 (258)	98 (102)	72 (198)	110 (186)	46 (215)
Total positive detection (%)	57.8	96.1	36.4	59.1	21.4

* The number preceding the parentheses is the number of sites with positive detections.
The number in parentheses is the total number of sites in the district.

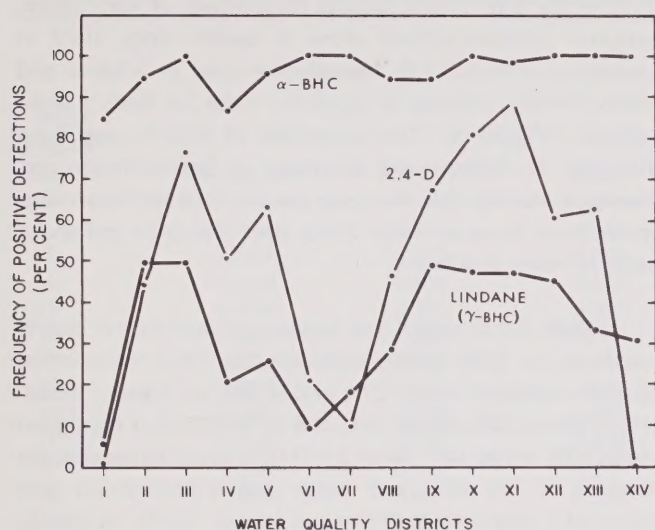


Figure 3. The frequency of detectable α -BHC, lindane (γ -BHC), and 2, 4-D in the various water quality districts.

Alpha-BHC has few or no insecticidal characteristics (Faust, 1972) and therefore is not an active ingredient in any pesticide product. It is, however, an impurity in the lindane product, but at less than 1%. N. Bostanian (Canada Department of Agriculture, personal communication) states that at one time entomologists viewed BHC as more effective than lindane and therefore BHC was used more extensively. BHC is composed of 60% to 70% alpha, 5% to 6% beta, 12% to 16% gamma, 5% to 7% delta and 2% to 3% epsilon isomers (Canada Department of Agriculture, 1967). J. Stocker (Canada Department of Agriculture, personal

communication) confirms that BHC (mixed isomers) was last registered in Canada in 1972, yet α -BHC is observed on a wide geographic scale and in quantities greater than would be expected on the basis of past use and impurity levels in the present lindane products.

Table 5 shows that more than 84% of the tests performed for α -BHC in each district were above the analytical detection limit of $0.001 \mu\text{g/L}$, with individual district maximums generally in the vicinity of $0.010 \mu\text{g/L}$. The maximum level of α -BHC recorded is $0.020 \mu\text{g/L}$ in district XI. Approximately 96% of the stations monitored (Table 4) and 85% of the tests performed in the remote Mountain district (I) were found to contain α -BHC (Table 5); 58% of the stations monitored and 6% of the tests performed were positive for lindane. The Canadian Shield district (XIV) also demonstrates residuals of lindane and α -BHC. Neither lindane nor α -BHC have been used in these districts in significant enough quantities to explain their detections; hence, long range transport and ultimately atmospheric deposition, must be the mechanism by which these organochlorine residues contaminate the surface waters in these remote districts. Oloffs *et al.* (1972) have suggested that atmospheric transport might, under certain conditions, account for the global redistribution of lindane.

A study of organics in precipitation across Canada was initiated in 1977 by the Water Quality Branch in cooperation with Atmospheric Environment Service of the Canadian Department of the Environment. The first results of the study, for July 1977, show precipitation at Edson, Alberta containing $0.074 \mu\text{g/L}$ α -BHC and $0.022 \mu\text{g/L}$

Table 5. Alpha-BHC Concentrations ($\mu\text{g/L}$) in Surface Waters of Western Canada.

Water Quality Districts	Statistics				Frequency of Possible Detections % (No.)	Number of Values Less Than Detection	Total Number of Tests
	Minimum	Maximum	Mean*	Median			
I	<.001	0.010	0.003	0.002	84.6 (55)	10	65
II	<.001	0.020	0.009	0.007	94.1 (16)	1	17
III	0.005	0.009	0.007	0.008	100.0 (4)	0	4
IV	<.001	0.010	0.004	0.005	86.6 (13)	2	15
V	<.001	0.009	0.004	0.004	95.5 (21)	1	22
VI	0.001	0.008	0.005	0.005	100.0 (8)	0	8
VII	0.002	0.005	0.004	0.005	100.0 (7)	0	7
VIII	<.001	0.007	0.003	0.005	94.1 (16)	1	17
IX	<.001	0.010	0.006	0.006	94.1 (16)	1	17
X	0.002	0.010	0.005	0.005	100.0 (9)	0	9
XI	<.001	0.010	0.006	0.006	98.2 (55)	1	56
XII	0.002	0.006	0.004	0.004	100.0 (18)	0	18
XIII	0.002	0.010	0.004	0.004	100.0 (19)	0	19
XIV	0.003	0.006	0.004	0.004	100.0 (5)	0	5

* The computation of the mean assumes "less than" values as real and equal to the analytical detection limit minus $0.0001 \mu\text{g/L}$.

lindane. Evidence of organochlorine contamination of the atmosphere has been reported elsewhere. Tarrant and Tatton (1968) report that organochlorine residues are frequently present in rainwater in the British Isles. In England, rainwater collected from two sites near London contained from 0.015 $\mu\text{g/L}$ to 0.040 $\mu\text{g/L}$ α -BHC and from 0.020 $\mu\text{g/L}$ to 0.155 $\mu\text{g/L}$ lindane (Morrison, 1972). Wide-spread detection of lindane and α -BHC has been reported in surface waters of Israel at levels as high as 0.04 $\mu\text{g/L}$ and 0.119 $\mu\text{g/L}$, respectively (Kahanovitch and Lahau, 1974). In this last example the author suggests atmospheric transportation as one mechanism responsible for the surface water contamination.

Characteristics such as volatility, metabolic rate, and solubility may account for the generally fewer detections of lindane than α -BHC. The reported isomerization of lindane to α -BHC in the environment (Sethanathan, 1973; Benezet and Matsumura, 1973) may partially explain the higher than expected levels of α -BHC observed in the surface waters monitored.

Although agriculture is the predominant source of lindane and α -BHC contamination of freshwaters in western Canada, urban centres and industry (packaging and manufacturing plants) are additional potential sources. During a 2,4-D survey of the Red River during July 1977 (discussed in the following section), the effluents from the City of Winnipeg's North End Pollution Control Centre and South End Pollution Control Centre were found to contain lindane at concentrations of 0.10 $\mu\text{g/L}$ and 0.08 $\mu\text{g/L}$, respectively.

Lindane is known to bioaccumulate in the food chain. It has been recommended (Great Lakes Water Quality Board, 1974) that lindane in water should not exceed 0.01 $\mu\text{g/L}$ for the protection of aquatic life. Tests for lindane and α -BHC conducted in 1976 on fish and wildlife in Alberta have been reported (Alberta Department of Agriculture, 1977) as 0.734 mg/L, and 0.150 mg/L to 0.282 mg/L, respectively. Although there is little information on the toxicity of α -BHC, this isomer is recognized as being more persistent, but less toxic, than the gamma isomer.

Chlorophenoxy Acid Herbicides

In western Canada, MCPA, 2,4-D and 2,4-DP are widely used on cereal crops for the control of broadleaf weeds; 2,4,5-T and 2,4-D are used for brush control in pastures. The chlorophenoxy acid herbicides, 2,4-D and MCPA account for more than 90% of the total herbicides used (Grover, 1974). Agricultural use patterns for the period

1972 to 1976 (F. Holm, Canada Department of Agriculture, personal communication) show a decline since 1972 in quantities of the 2,4-D formulation used in Alberta and Saskatchewan, whereas in Manitoba there has been a slight increase (Figure 4). The quantities of MCPA used have increased in Alberta and decreased in Saskatchewan and Manitoba during this five-year period. Saskatchewan uses about three times as much 2,4-D than Manitoba and about twice as much as Alberta.

Both 2,4-D esters and amines are used in the prairie provinces. In 1976 in Saskatchewan, the 2,4-D formulation applied contained about 27% amine salt, in Alberta it contained about 33% amine salt, and in Manitoba it contained about 81% amine salt. Since 2,4-D (free acid) is a breakdown product of the salts and esters and is biologically and chemically more stable (Paris and Lewis, 1973), its fate in the aquatic environment is of concern.

Positive detections of 2,4-D have been frequently observed in most of the 14 water quality districts (Table 6 and Figure 3). The highest frequencies of positive detections were found in those districts in and overlapping the agricultural areas of Saskatchewan. The remote areas I and XIV showed 1% and no positive detections for 2,4-D, respectively. This is contrary to the observation for lindane and α -BHC, which are prevalent in the surface waters of these areas.

The lack of 2,4-D in the remote surface waters can be explained in part by (1) the relatively short persistence of 2,4-D, (2) the limited use of this herbicide in the remote districts and (3) possibly the volatility (atmospheric mobility) of 2,4-D formulations. Grover (1974) reports that air monitoring to determine herbicidal drift near Regina, Saskatchewan detected esters of 2,4-D whereas residues of the amine salt were undetectable. He states that the predominant form of 2,4-D in the air is the highly volatile butyl ester. The significance of this observation is that the mechanism of atmospheric contamination of surface waters appears to be dependent to some extent on the herbicide formulation. In Manitoba, which uses large quantities of the non-volatile amine salt, contamination derived from the atmosphere is primarily from direct non-target application of the herbicide and from drift within short distances of herbicide application. In Alberta and Saskatchewan, where 2,4-D ester formulations are used extensively, atmospheric contamination of surface waters probably results from direct non-target application, drift, and long range transport within the degradation life time of 2,4-D. Although atmospheric transportation helps account for the geographic distribution of 2,4-D, the rapid breakdown of 2,4-D probably precludes anything more than periodic detection of 2,4-D in surface waters that are remotely situated (as waters in districts I and XIV) from the areas of herbicide use.

Table 6. 2,4-D Concentrations ($\mu\text{g/L}$) in Surface Waters of Western Canada.

Water Quality Districts	Statistics						
	Minimum	Maximum	Mean*	Median	Frequency of Positive Detections % (No.)	Number of Values Less Than Detection	Total Number of Tests
I	<.004	0.025	<.004	<.004	1.1 (6)	548	554
II	<.004	0.080	0.020	<.004	44.7 (17)	21	38
III	<.004	0.106	0.054	0.061	76.9 (10)	3	13
IV	<.004	0.095	0.013	0.004	50.9 (30)	29	59
V	<.004	0.248	0.005	0.016	63.1 (53)	31	84
VI	<.004	0.090	0.010	<.004	20.9 (9)	34	43
VII	<.004	0.010	0.004	<.004	10.0 (2)	18	20
VIII	<.004	0.228	0.015	<.004	46.2 (24)	28	52
IX	<.004	0.334	0.035	0.019	67.2 (37)	18	55
X	<.004	4.33	0.235	0.040	80.6 (54)	13	67
XI	<.004	0.60	0.038	0.020	89.0 (187)	23	210
XII	<.004	3.40	0.101	0.010	60.4 (32)	21	53
XIII	<.004	0.070	0.016	0.008	62.9 (73)	43	116
XIV	<.004	<.004	<.004	<.004	0.0 (0)	22	22

* The computation of the mean assumes "less than" values as real and equal to the analytical detection limit minus 0.0001 $\mu\text{g/L}$.

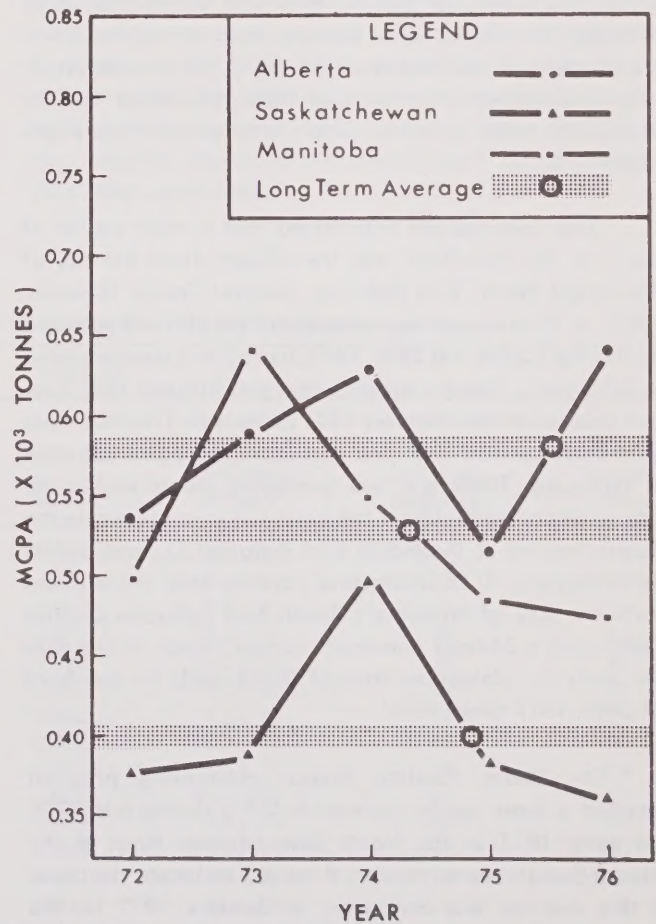
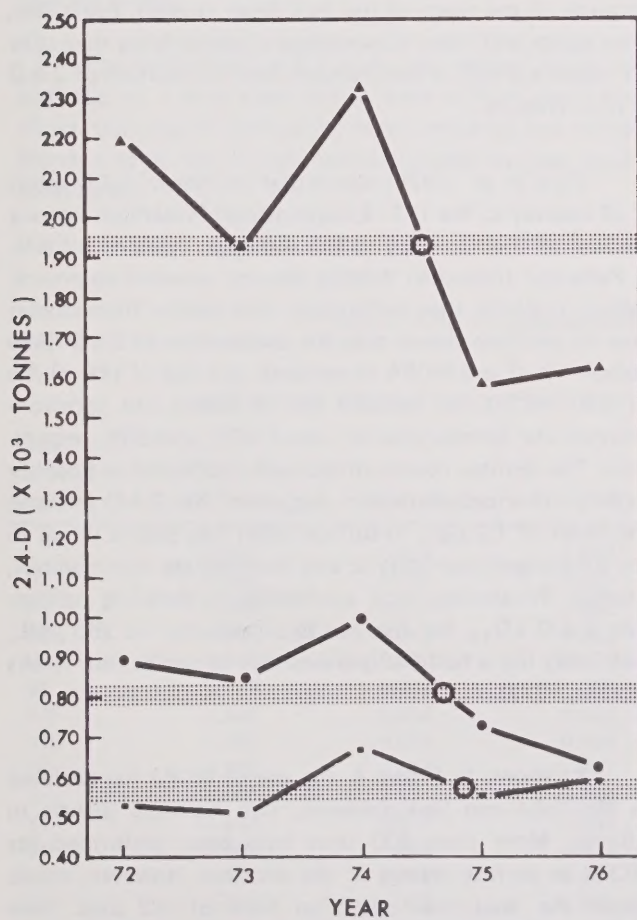


Figure 4. Use patterns of 2, 4-D and MCPA in the Prairie Provinces.

In the rural areas, slight seasonal variation in 2,4-D concentrations are discernible from the detailed data, with the higher levels generally detected during the period from May to September, which corresponds to the normal period of 2,4-D application. Occasional high levels were observed in the winter periods. This is not surprising, considering that the degradation of 2,4-D is inhibited by colder temperatures and lower dissolved oxygen (Paris and Lewis, 1973). Throughout the entire monitoring period 1971 to 1977, 59% of the stations sampled had detectable 2,4-D on one or more occasions. Of the total number of 2,4-D tests (1386) performed, 39% were positive, but if those districts remote from direct agricultural influence (I, VI, XII and XIV) are excluded, 69% of the tests performed had detectable 2,4-D.

It is readily apparent from the results of the monitoring programs that there is a significant contribution of 2,4-D to the aquatic environment via municipal and industrial effluents. The highest 2,4-D values on record occurred at sites below urban centres. A maximum level of 4.33 $\mu\text{g/L}$ was recorded in Wascana Creek below the city of Regina, Saskatchewan (in district X) during January 1974; and in February of 1977, a maximum of 3.40 $\mu\text{g/L}$ was recorded in the Red River near Selkirk, Manitoba, below the city of Winnipeg (in district XII). Because both the winter 2,4-D maximum and the magnitude of the 2,4-D concentration were unprecedented in the Red River, the Water Quality Branch conducted an investigation to determine the primary source of 2,4-D.

This investigation determined that a major source of 2,4-D to the Red River was the effluent from the city of Winnipeg's North End Pollution Control Centre (Chacko, 1977). A 24-hour composite sample of the effluent collected during April 27th and 28th, 1977, had a 2,4-D concentration of 30.5 $\mu\text{g/L}$. Chacko suggests that this effluent may have also resulted in the February 1977 maximum. The maximum level corresponded with the herbicide packaging activities in Winnipeg. There are two packaging plants within the city of Winnipeg that have the potential to contaminate the water received at the North End Pollution Control Centre for treatment. It is interesting to note that the effluent from the city of Winnipeg's South End Pollution Control Centre had a 24-hour composite concentration of less than the analytical detection limit of 0.004 $\mu\text{g/L}$ for the April 27-28th, 1977 time period.

The Water Quality Branch monitoring program detected a more subtle increase in 2,4-D during late 1976 and early 1977 in the North Saskatchewan River at the Alberta-Saskatchewan border. A survey to locate the cause of this increase was conducted in January 1977 by the Alberta Department of Environment. The survey revealed 2,4-D levels as high as 4.34 milligrams/litre in the effluent

from a Uniroyal Limited plant located a few kilometres east of Edmonton, Alberta (P. Grant, Alberta Department of Environment, personal communication). The river monitoring site at which the increase in the North Saskatchewan River was first detected is approximately 280 km downstream from this effluent.

Most pesticides have a strong tendency to be adsorbed on suspended matter, on sediments and other surfaces. Hurlbert (1975) has reported that following an application of 112 kg/ha of 2,4-D, the concentration of 2,4-D in water dropped below 1 $\mu\text{g/L}$ in eight hours. Four days after treatment, bottom sediment had 2,4-D residues ranging from 0.950 mg/kg to 56.0 mg/kg; ten months after treatment, sediment had 2,4-D residues ranging from 0.240 mg/kg to 58.0 mg/kg. Contrary to these earlier findings, one to two days after applying 148 mL/ha to 590 mL/ha of 2,4-D (low volatile ester), the 2,4-D concentrations in the water phase were 10 $\mu\text{g/L}$ to 15 $\mu\text{g/L}$ and no 2,4-D was observed in bottom sediment (J. Patterson, Canadian Wildlife Service, personal communication). In work conducted by Chacko (1977), 2,4-D was not found in Red River bottom sediment which suggests that 2,4-D was in solution or associated with the suspended sediments and thus held in suspension throughout the reach of the Red River studied. Flow rate, river depth and other flow-related characteristics may play an important role in the transport and distribution of 2,4-D in river systems.

Zepp *et al.* (1975) report that the fate of 2,4-D esters is of interest to the U.S. Environmental Protection Agency because of their toxicity to fish and other types of wildlife. J. Patterson (Canadian Wildlife Service, personal communication) indicates that preliminary information from studies now in progress shows that the application of 2,4-D (low volatile ester) and MCPA to wetlands at a rate of 148 mL/ha to 590 mL/ha has reduced the herbivore and carnivore invertebrate communities by about 40%, and 80%, respectively. The detritus communities were unaffected or possibly slightly enhanced. Patterson suggested that 2,4-D levels in the order of 1.0 $\mu\text{g/L}$ in surface water may pose a threat to the submerged macrophytic and invertebrate communities, thereby threatening food availability in duckling habitat. The 2,4-D LD_{50} for fish has been reported as 250 $\mu\text{g/L}$, and 2,4-D has a half-life (persistence) of one to four weeks (Weber, 1977).

As shown in Figure 4, the use of MCPA has declined in Manitoba and Saskatchewan, but increased slightly in Alberta. More than 400 tests have been performed for MCPA in surface waters of the districts. However, values above the analytical detection limit of 0.2 $\mu\text{g/L}$ have not been observed. The preliminary work of Patterson (Canadian Wildlife Service, personal communication) has

revealed that MCPA migrates rapidly from the water to the bottom sediments. This phenomenon may help explain why MCPA has gone undetected during monitoring of the water phase. In addition, the high detection limit (1000 times higher than that for 2,4-D) may have precluded an adequate evaluation of MCPA in the surface waters during the monitoring period.

The ester and amine compounds of the herbicide 2,4,5-T are used regionally. Statistics on how much has been, and is used, are not available; however, quantities are known to be relatively small compared to 2,4-D quantities. Nevertheless, 48% of the tests performed in the Qu'Appelle River district (X) and 22% of the tests performed in the North Saskatchewan River district (V) were positive for 2,4,5-T (Table 7). All other districts had less than 15% positive detections. The maximum value recorded is 3.12 µg/L in district X. Of the total number of sites monitored (198), 36% had at least one positive detection. Weber (1977) reports the LD₅₀ for 2,4,5-T to fish to be 500 µg/L and the half-life (persistence) to be 1 to 12 weeks. Kenaga (1975) reviewed the stability of esters of 2,4,5-T in the aquatic environment, and found them to be rapidly hydrolyzed in most waters with the exception of those that are acidic.

The herbicide 2,4,5-T does not appear to be problematic on a wide scale, but in areas of high use it could affect the aquatic habitat of local wetlands and sloughs. Monitoring by the Branch has not focused on these aquatic ecosystems.

Dichloroprop, or 2,4-DP, is not used in as large quantities as 2,4-D or MCPA. Most often it is used in conjunction with 2,4-D rather than alone for the control of broadleaf weeds in wheat and barley crops.

Dichloroprop is not as prevalent as 2,4-D in the surface waters of western Canada (Table 8). Twenty-one per cent of the stations monitored recorded positive detections one or more times, and only 5% of 1455 tests were above the analytical detection limit of 0.004 µg/L. The maximum level recorded in surface waters of western Canada was 7.15 µg/L in district X (Table 8). This district accounted for 50% of the total positive detections. Dichloroprop is more persistent than 2,4-D (J. Holm, Saskatchewan Department of Agriculture, personal communication) and is harmful to pollinating insects such as bees and bumblebees (Makkula, 1975).

Organophosphorus Insecticides

These insecticides do not constitute part of the Branch's routine monitoring programs. Approximately 100 tests were performed during the summers of 1973 and 1974 for each of Guthion, malathion and dimethoate. Grab samples for these organophosphorus insecticides were collected from surface waters located within and contiguous to areas sprayed with these chemicals. Examination of surface waters for organophosphorus insecticides has not been performed since 1974. As previously mentioned, they degrade rapidly in the environment and, as a result, have gone undetected.

Table 7. 2,4,5-T Concentrations (µg/L) in Surface Waters of Western Canada

Water Quality Districts	Statistics						
	Minimum	Maximum	Mean*	Median	Frequency of Positive Detections % (No.)	Number of Values Less Than Detection	Total Number of Tests
I	<.002	0.014	<.002	<.002	2.0 (11)	541	552
II	<.002	0.008	0.002	<.002	2.6 (1)	37	38
III	<.002	0.002	<.002	<.002	7.7 (1)	12	13
IV	<.002	0.015	<.002	<.002	5.9 (5)	79	84
V	<.002	0.020	0.003	<.002	22.2 (20)	70	90
VI	<.002	0.040	<.002	<.002	9.3 (4)	39	43
VII	<.002	0.002	<.002	<.002	5.0 (1)	19	20
VIII	<.002	0.071	0.004	<.002	13.2 (7)	46	53
IX	<.002	0.013	<.002	<.002	5.3 (3)	53	56
X	<.002	3.12	0.090	<.002	48.3 (42)	45	87
XI	<.002	0.071	<.002	<.002	3.5 (7)	190	197
XII	0.002	<.002	0.003	<.002	13.2 (7)	46	53
XIII	<.002	0.020	0.003	<.002	6.7 (8)	110	118
XIV	<.002	<.002	<.002	<.002	0.0 (0)	22	22

* The computation of the mean assumes "less than" values as real and equal to the analytical detection limit minus 0.0001 µg/L.

Table 8. 2,4-DP Concentrations ($\mu\text{g/L}$) in Surface Waters of Western Canada.

Water Quality Districts	Statistics				Frequency of Positive Detections % (No.)	Number of Values Less Than Detection	Total Number of Tests
	Minimum	Maximum	Mean*	Median			
I	<.004	0.016	<.004	<.004	0.4 (2)	563	565
II	<.004	0.028	0.005	<.004	6.6 (2)	28	30
III	<.004	<.004	<.004	<.004	0.0 (0)	15	15
IV	<.004	0.007	<.004	<.004	1.7 (1)	57	58
V	<.004	0.033	0.005	<.004	8.6 (6)	64	70
VI	<.004	0.044	<.004	<.004	6.5 (3)	43	46
VII	<.004	<.004	<.004	<.004	0.0 (0)	16	16
VIII	<.004	0.038	0.005	<.004	6.1 (3)	46	49
IX	<.004	0.028	<.004	<.004	7.4 (4)	50	54
X	<.004	7.15	0.233	<.004	35.3 (42)	77	119
XI	<.004	0.027	<.004	<.004	1.8 (4)	223	227
XII	<.004	0.131	0.009	<.004	5.1 (3)	56	59
XIII	<.004	0.030	0.004	<.004	0.8 (1)	117	118
XIV	<.004	<.004	<.004	<.004	0.0 (0)	29	29

* The computation of the mean assumes "less than" values as real and equal to the analytical detection limit minus $0.0001 \mu\text{g/L}$.

Carbamate Insecticides

Significant amounts of carbamate insecticides are not used in the Prairies; consequently, there has been limited monitoring of these insecticides in surface waters. As a result of a potential outbreak of the western encephalomyelitis virus in Manitoba during the summer of 1975, Baygon was applied aerially to control the adult mosquito. Twenty-five samples for Baygon analysis were collected and analyzed from surface waters in and around the city of Winnipeg, Manitoba. Of the total number of samples analyzed, 50% were positive for Baygon (Gummer, 1975). The highest level, $36.4 \mu\text{g/L}$, was recorded in Sturgeon Creek in the city of Winnipeg about 12 hours after aerial application. Four samples from the La Salle River had levels in excess of $17.5 \mu\text{g/L}$.

The biodegradation of Baygon is quite rapid, particularly in waters with high bacterial activity and elevated temperatures. The colder water temperatures (15°C) that occurred during the latter days of aerial application may have slightly retarded the otherwise rapid degradation.

Carbofuran is used in western Canada for the control of grasshoppers. Monitoring of this carbamate has been limited, amounting to about 60 samples collected during 1974-1975. All the tests conducted revealed no concentrations at or above the analytical detection limit of $1.0 \mu\text{g/L}$. In 1974, the Branch participated in a special cooperative study with Agriculture Canada to investigate the residual carbofuran levels in an aquatic environment (a slough) aerially sprayed with carbofuran. The results of the study

indicated no identifiable residues of carbofuran or hydroxy-carbofuran in soil, water, or bottom muds immediately after spraying, or at 1, 7 and 16 days after treatment (Ormrod, 1976). This experiment suggests rapid degradation of carbofuran and further suggests that routine monitoring in western Canada would not detect residual carbofuran levels in surface waters.

SUMMARY

The monitoring of surface waters in western Canada has revealed that the chlorophenoxy acid herbicides 2,4-D; 2,4-DP; and 2,4,5-T as well as the organochlorine pesticides lindane and α -BHC are frequently detected. Lindane has been found on occasion to exceed the limit of $0.01 \mu\text{g/L}$ prescribed by the Great Lakes Water Quality Board (1974) for the protection of aquatic life. The herbicide 2,4-D has been found in water at levels in excess of $1.0 \mu\text{g/L}$, which may be detrimental to the invertebrate community.

The highest concentrations of 2,4-D; 2,4-DP; 2,4,5-T; and lindane were recorded in the Qu'Appelle River district (X), which probably reflects the more intense agricultural activity in this district. Sampling sites below large urban and industrial centres such as Winnipeg, Regina and Edmonton confirm that substantial quantities of pesticides are introduced to the environment via municipal and industrial effluents. No seasonal patterns were discernible at these locations, whereas the high levels in the rural regions were generally observed to correspond to the May – September herbicide application period.

Alpha-BHC commonly occurs in waters throughout all of the districts at levels in excess of $0.001 \mu\text{g/L}$. Although α -BHC is not presently viewed as a problem to the aquatic community, because of its prevalence the need exists to define the toxicological properties of this substance more fully. Its prevalence is thought to result from the extensive past agricultural use of technical-grade BHC, impurities in presently used lindane products and the isomerization of γ -BHC (lindane) to α -BHC. The wide geographic dispersion of both lindane and α -BHC beyond the areas of use, suggests that atmospheric transport and deposition are key factors in the environmental distribution of these pesticides. The data suggest that the chlorophenoxy acid herbicides are less volatile and degrade faster than the organochlorine pesticides and therefore are not found as extensively.

Carbamate insecticides are not routinely monitored in western Canada. Baygon monitoring during and after an emergency spray program in Manitoba showed levels as high as $36.4 \mu\text{g/L}$ 12 hours after application. A special study investigating residual levels of carbofuran in an aquatic environment suggests that carbofuran degradation is rapid and that residual levels would therefore not likely be detected in a monitoring program.

Sediment (benthic) investigations for pesticides have not been conducted by the Branch as part of the routine monitoring programs. However, the Branch has undertaken steps to increase its activities in monitoring for pesticides in suspended and deposited sediments, and aquatic organisms.

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